Studies on the Rate of Reaction CH and CO. (III)

AUTHOR(S):

Tarama, Kimio; Hayakawa, Syuichi

CITATION:

Tarama, Kimio ...[et al]. Studies on the Rate of Reaction CH and CO. (III). 京都大学化学研究所報告 1951, 26: 86-87

ISSUE DATE:

1951-12-10

URL:

http://hdl.handle.net/2433/74313

Tab. 3. Influence of contact time.
(Catalyst: MgO; Reaction temp.: 350°C)

Time sec.	F・A	R	A/F	k_1/k_2
18	0.500	0.074	1.13	1.04
24.5	0.482	0.104	1.19	0.94
39	0.400	0.137	0.77	0.68

25. Studies on the Rate of Reaction CH_4 and CO_2. (III)

Kimio Tarama and *Syūichi Hayakawa*

(Kodoma Laboratory)

The rate of thermal reaction of CH_4 and CO_2 was investigated at 1147−1236°K and 100−300 mmHg in which the pressure change caused by the reaction was determined and the reaction product was analysed with a modified Ambler's apparatus.

In the earlier stage of the reaction, H_2 is mainly formed, as the result of a mere decomposition of CH_4 and in the laler stage CO is formed due to the reaction of CO_2 and H_2 which increased rapidly as the reaction proceeds, but the amounts of CO are always smaller than those of H_2.

At constant intial pressures of CH_4, the amounts of H_2 produced are scarecely affected by the initial pressures of CO_2, but contrarily those of CO change regularly with the initial CO_2 pressure. On the other hand, both amounts of H_2 and CO increase conspicuously with the initial CH_4 pressure when the initial pressures of CO_2 are constant.

In the earlier stage of the reaction, the rate of pressure change is the 1st order with respect to the partial pressure of CH_4, while the rate of CO formation is always approximately 1st order respecting partial pressure of CO_2.

On the basis of the results of these experiments and the previous investigations on the rates of the reaction of $CO_2+H_2=CO+H_2O$ and $C+CO_2=2CO$, the following mechanism is proposed:

$$CH_4 \xrightarrow{k_1} C\ (ad)+2H_2$$

$$CO_2 \underset{r_2}{\overset{k_2}{\rightleftarrows}} CO_2(ad)$$

$$CO_2(ad)+H_2 \xrightarrow{k_3} CO+H_2O(ad)$$

$$C(ad)+H_2O(ad) \xrightarrow{k_4} CO+H_2$$

$$C(ad)+CO_2(ad) \xrightarrow{k_5} 2CO$$

k : velocity constant

(ad): represents the adsorbed state on the reaction vessel surface.

The following equation for the rate of CO formation can be derived from this mechanism with the assumptions that the adsorption of CO_2 exists always in an equilibrium and $k_5 \ll k_3 \ll k_4$,

$$\frac{d[CO]}{dt} = \frac{2\,k_2\,[H_2]}{r_2/k_3+[H_2]}[CO_2],$$

which reproduces our experimental results approximately.

---

26. Syntheses of Antioxidants for Fats and Oils. II Cresol-analogs of NDGA and Polynuclear Phenolic Antyioxidants

Keiiti Sisido and *Hirosi Kuyama*

(Sisido Laboratory)

The two cresol-analogs of NDGA were prepd. The Grignard reagent of p-bromo-o-cresol methylether was condensed with allyl bromide to p-methoxy-m-methylallylbenzene (I), b_{12} 132–142°. The Grignard reagent of the hydrobromide of (I), b_{13} 132–140°, was treated with I_2, giving meso and racemic mixt. of 1,4-bis (p-methoxy-m-methylphenyl)-2,3-dimethylbutane, b_5 210–215°, meso m. 79–80°. On demethylation with MeMgI and recryst. from benzene, free phenol (II), m. 80–81°, was obtained. p-Cresol allyl ether was rearranged and then methylated to 2-methoxy-5-methylallylbenzene (III), b_{45} 131–132°. Hydrobromide of (III), b_{13} 138–142°, was treated as above, giving 1,4-bis(2-methoxy-5-methylphenyl)-2,3-dimethylbutane, b_{2-3} 195–200°, meso m. 91°, free phenol (IV) m. 163–4°.

The following hindered phenol antioxidants having large molecular size were prepd. The mixt. of 10 g. of 2,6-dimethylol-p-cresol and 39 g. of phenol in 50 ml. of 60% ethanol was saturated with HCl gas at 0°. On standing overnight there resulted white crystals which were filtered and 12 g. of condensate (V), recryst. from acetic acid m. 211–12°, acetate m. 117–18°, was obtained. The determination of the structure is now under way. 2,6-Dimethylol-p-cresol and p-cresol gave crystalline condensate (VI), m. 210–11°, which has probably a four nuclear cyclic structure according to J. B. Niedrel (J. Am. Chem. Soc. **65** 629 (1943)). On similar treatments o-cresol, thymol and eugenol gave amorphous solids (VII), (VIII) and